

**EPA*****SITE Technology Capsule*****J.R. Simplot Ex-Situ Anaerobic
Bioremediation Technology: TNT****Abstract**

The J.R. Simplot Ex-Situ Bioremediation Technology, also known as the J.R. Simplot Anaerobic Bioremediation (SABRE™) process, is designed to anaerobically degrade nitroaromatic and energetic compounds with total destruction of toxic intermediate compounds at the completion of treatment. An evaluation of this technology was conducted under the SITE Program on soils contaminated with 2,4,6-trinitrotoluene (TNT) at the Weldon Spring Ordnance Works (WSOW) site. This SITE Demonstration utilized 23 m³ (30 yd³) of TNT-contaminated soil mixed with water to form a slurry in a 1:1 ratio (by weight) to evaluate the effectiveness of this technology. The Demonstration was conducted over the 1993 winter, when freezing conditions existed for five mo of the Demonstration Test. To offset these below zero temperatures, heaters were added to the bioreactor to keep the slurry from freezing.

The Reduction Efficiency based on the TNT pre-treatment slurry concentration of 1,500 mg/kg (dry basis) and the TNT post-treatment slurry concentration of 8.7 mg/kg (dry basis) was 99.4% with a 95% Confidence Interval of 98.3% to 99.9%. The treatment time associated with this Reduction Efficiency was approximately 9 mo. A Reduction Efficiency of 95% (the developer's claim) was achieved in approximately 5 mo. The treatment time is considered to be a function of the bioreactor slurry temperature and the initial average TNT concentration, among other factors. Intermediate byproducts (amino and diamino derivatives, p-cresol, and 2,4,6-trihydroxytoluene) were found to increase at the start of treatment and then decrease to below the analytical detection limit at the completion of treatment.

Relative toxicity testing of the slurry before treatment and at a point 5 mo after the commencement of treatment was performed. This testing included early seedling growth, root elongation, and earthworm survival and reproduction tests. The results of this testing, after the 95% Reduction Efficiency was reached, showed that the soil was reduced in toxicity.

The Simplot technology was evaluated based on the seven criteria used for decision-making in the Superfund Feasibility Study (FS) process. Results of this evaluation are summarized in Table 1.

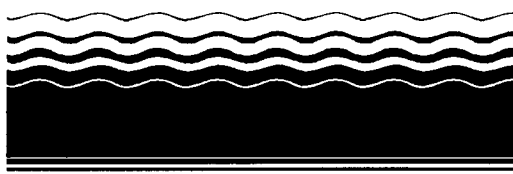
Introduction

This Capsule evaluates the J.R. Simplot Ex-Situ Bioremediation Technology on the treatment of TNT-contaminated soil. This process is designed to degrade nitroaromatic and energetic compounds in soil and water. An earlier Demonstration evaluated the technology to biodegrade the listed herbicide (P020), 2-sec-butyl-4,6-dinitrophenol (dinoseb). The second Demonstration of this technology, the focus of this Capsule, was conducted under the SITE Program from September 1993 to June 1994 at the WSOW site near St. Louis, MO. The contamination at this site can be traced to former production methods at the WSOW. The J.R. Simplot Company teamed with Envirogen Inc. to demonstrate this technology at the WSOW site. This Capsule presents the following information:

- Technology Description
- Technology Applicability
- Technology Limitations
- Process Residuals
- Site Requirements
- Performance Data
- Summary of Results
- Economic Analysis
- Technology Status
- SITE Program
- Sources of Further Information

Technology Description

The J.R. Simplot Company has developed a procedure that treats soils contaminated with nitroaromatic and other energetic compounds by the enhancement of naturally selected anaerobic soil microorganisms. These microorganisms were not found to be indigenous to the WSOW site and TNT



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Table 1. Evaluation Criteria for the J.R. Simplot Ex-Situ Bioremediation Technology: TNT

Criteria						
Overall Protection of Human Health & the Environment	Compliance with Federal ARARs	Long-Term Effectiveness	Short-Term Effectiveness	Reduction of Toxicity, Mobility, or Volume through Treatment	Implementability	Cost
Provides both short- and long-term protection by destroying contaminants in soil.	Requires compliance with RCRA treatment, storage, and land disposal regulations (for a hazardous waste).	Permanently destroys contamination and intermediates.	Presents potential short-term risks to workers and nearby community, including exposure to noise and contaminants released to air during excavation and handling. These can be minimized with correct handling procedures and borders.	Eliminates toxicity of soil contaminants through treatment.	Major equipment is limited to bioreactor and agitation/suspension devices.	\$147/m ³ (\$112/yd ³) for treatment in a small portable bioreactor and a total treatment volume of 23 m ³ (30 yd ³)
Prevents groundwater contamination and offsite migration.	Excavation, construction, and operation of onsite treatment unit may require compliance with location-specific ARARs.	Provides reduction in contamination levels; duration of treatment determines final contaminant levels.		Does not leave intermediates if conducted properly. Could result in intermediates if terminated prematurely.	Support equipment includes earthmoving equipment (for excavation, screening, and loading of bioreactor) and monitoring equipment (for tracking of pH, redox potential, and temperature).	\$718/m ³ of soil (\$549/yd ³) for treatment in an erected lined bioreactor and a total treatment volume of 956 m ³ (1,250 yd ³).
Requires measures to protect workers and perhaps nearby communities during excavation, handling, and treatment.	Emission controls may be needed to ensure compliance with air quality standards if volatile compounds are present.	Overall toxicity reduced between pre- and post-treatment.		If not fully dried, increases volume of treatment material by addition of water to create slurry.		\$405/m ³ (\$310/yd ³) for treatment in multiple erected lined bioreactors and a total treatment volume of 7,646 m ³ (10,000 yd ³).
	Wastewater discharges to POTW or surface bodies require compliance with Clean Water Act regulations.				Once onsite, the small portable bioreactor can be assembled and ready to load within 2 days. The larger modular bioreactor requires approximately 4 days. After excavation, bioreactor loading activities (soil and water) are a function of the treatment volume.	Actual cost of a remediation technology is dependent upon the volume of soil, soil characteristics, contaminants present, and the initial and target cleanup levels.
					After treatment is complete, the small bioreactor can be emptied and demobilized in 3 days. If allowed by enforcement personnel, treated soil can be placed in the excavated area and used as fill material. For erected bioreactors, the integrity of the liner can be intentionally breached when treatment is complete.	An additional cost of up to \$131/m ³ (\$100/yd ³) may be assessed to the client by the developer.

degraders were added to the slurry after the process became anaerobic. The Simplot process is initiated under aerobic conditions, but anaerobic conditions are quickly achieved under design parameters, thus enabling the microbes to degrade the nitroaromatic contaminants. In the case of TNT degradation, toxic intermediate compounds are evolved and then destroyed by the process.

At the WSOW site, contaminated soil was inoculated with microorganisms in a 0.02 m³ (a 5-gal pail) of WSOW soil that was previously remediated by the Simplot process during treatability studies.

The Simplot technology utilized a portable tank as the bioreactor during this Demonstration because of the small volume of test soil. The bioreactor for these tests was 12.2 m long, 2.4 m wide, and 2.6 m tall (40 ft x 8 ft x 8.5 ft), which approximates to 75,700 L (20,000 gal). In applications where larger volumes of soil are treated, one or more lined pits or erected lined tanks, both capable of remediating 956 m³ (1,250 yd³) of soil, may be used.

Initially, water was added to the bioreactor with the contaminated soil in sufficient quantity to provide a ratio of 1 L of water to 1 kg of soil. Nutrients (a J.R. Simplot Company potato-processing starch byproduct) and pH-regulating agents (buffers) were added to induce the aerobic microorganisms to thrive and consume oxygen from the soil. This point was considered day 0 in the remediation process. The nutrient and buffer addition helped lower the redox potential (E_h) and create anaerobic conditions. Anaerobic conditions with an E_h less than -200 mV promote the establishment of the anaerobic microorganisms capable of degrading nitroaromatic compounds.

Figure 1 shows the Simplot process flow diagram for the SITE Demonstration. The first step was to pass the excavated soil through a vibrating screen to remove rocks and other debris >15.9 mm (5/8") in diameter. This oversize was neglected for the purpose of this Demonstration Test. However, it may be possible to separate the contaminated fine material from the oversize using a soil/rock washing system, or, to crush this oversize to the required dimensions. If these options are not practical, then the oversize (if required) could be disposed of at a RCRA permitted disposal facility. Water was added to the bioreactor to provide the 1-L to 1-kg ratio required for treatment. A phosphate buffer solution was added to the system to control the pH to approximately 7. Batches of soil and the J.R. Simplot potato-processing starch byproduct were mixed together by hand and added to the bioreactor. This continued until all of the treatment soil was loaded into the bioreactor. The bioreactor was sized so that it was approximately 60% full when loaded.

At first, the bioreactor was loosely covered and underwent frequent lancing to mix together the soil and water. The lancing was accomplished by placing the suction end of a diaphragm pump into the treated portion of the bioreactor and pumping it into the sediment portion of the bioreactor. After approximately 2 mo, three electrical immersion heaters were added to the system and a solar blanket was placed over the slurry due to the cold weather that was encountered during the winter of 1993-94. Lancing continued at the rate of once every 1 to 2 wk. The bioreactor was equipped with instrumentation to monitor pH, temperature and redox potential of the slurry. Laboratory testing by the developer found optimum operating conditions for the degradation of TNT to be temperatures between 35 and 37°C, a pH below 8 (ideally between 6.0 and 7.0), and a redox potential lower than -200 mV (1).

Technology Applicability

The J.R. Simplot Ex-Situ Bioremediation Technology is a stand-alone system that can be used to biodegrade nitroaromatic and energetic compounds in solid and liquid matrices. Simplot claims that any type of soil can be treated, providing that the treatment slurry is thoroughly mixed with the carbon-based nutrients. Under optimum laboratory conditions, the rate limiting step within this process is the diffusion of the nitroaromatic compounds from the solid phase to the liquid phase. Sufficient temperatures must be maintained to avoid freezing conditions. If the soil to be treated contains rocks or debris greater than approximately 38.1 mm (1-1/2") in diameter, then the technology must be used with either a rock/soil washing system or a rock crushing device. The soil type used during the Demonstration Test was a clayey gravel with sand. The soil itself need not contain the necessary microorganisms to degrade the nitroaromatic since the bioreactor can be inoculated with the appropriate microorganisms. These microorganisms can be obtained from previous remediations or treatability studies.

Technology Limitations

This technology is suitable for a variety of soil types that are contaminated with nitroaromatic and energetic compounds. However, if a large percentage of the soil contains rocks or debris >38.1 mm (1-1/2") diameter, then either the contaminants must be removed from these large particles by a separate technology, or the large particles may be crushed to the required size and added to the bioreactor for treatment.

As with any biodegradation technology, the presence of high concentrations of metals may be toxic to the microorganisms. However, the process is a sulfate-reducing process, therefore, toxic metals are reduced to their sulfide form, making them less toxic to the microorganisms. Another limiting factor is that hydrocarbon concentrations greater than 1,000 mg/kg Total Recoverable Petroleum Hydrocarbons (TRPH), by weight, are thought to be toxic to the microorganisms.

The degradation of TNT using this bioremediation technology does not appear to be as temperature dependent as other biological systems. However, degradation rates can be slowed if suboptimum temperatures exist. This problem can be overcome by adding heaters to the system.

Process Residuals

The process waste streams generated by the J.R. Simplot Ex-Situ Bioremediation Process are any potential oversize (>38.1 mm) rocks or debris. For the purposes of this Demonstration Test, the system was required to achieve the cleanup goals set by the Missouri Department of Natural Resources (MDNR). The Simplot technology had to reduce the level of TNT to below 57 mg/kg and maintain a total sum of the known toxic intermediate compounds at each sampling location to below 2.5 mg/kg. At the completion of treatment, the entire contents of the bioreactor were placed in lined pits to await final disposition.

The Simplot Company proposes to return treated soil to the excavated areas as fill material if the treatment standards have been met. In states where cleanup levels have not been established or when cleanup levels have not been met, then disposal of the soil at a RCRA-permitted facility may be necessary. If a nitroaromatic compound other than TNT is remediated, disposal of the soil at a RCRA-permitted facility is required only if the compound is a listed waste or has hazardous waste characteristics.

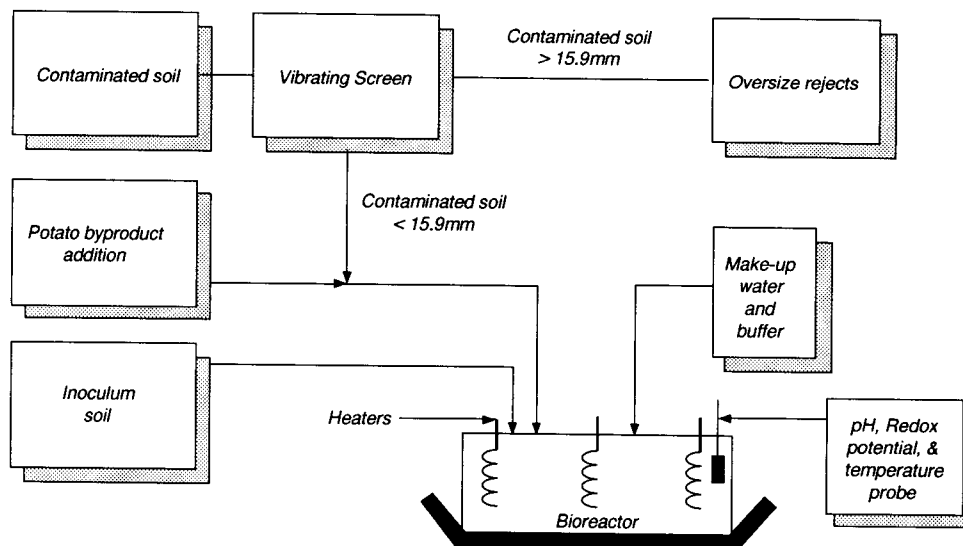


Figure 1. J.R. Simplot process flow diagram: TNT.

The water used to form the slurry and any rinse water used to wash the rocks or debris (and subsequently added to the bioreactor for treatment) can be disposed through the local sewer system if all treatment standards have been met. If treatment standards have not been met, the liquid must be disposed of at a RCRA-permitted facility.

The oversized rocks or debris, if not washed or crushed, may require formal disposal procedures at a RCRA-permitted facility if treatment standards are not met. If the washed or crushed rocks and debris are shown to meet the treatment standards, they may also be used as fill material in the excavated areas.

Site Requirements

The site requirements for the J.R. Simplot Ex-Situ Bioremediation Technology are a function of the quantity of soil to be treated. If up to 31 m³ (40 yd³) or less of soil is to be remediated, then a small 75,700-L, (20,000-gal) portable bioreactor may be used. If the site contains greater than 31 m³ of contaminated soil, then inground pits to a depth of 1.2 m (4 ft) with a 1-ft berm can be constructed, or, one or more lined erected bioreactors can be used. Equipment requirements are limited to front-end loaders and backhoes for excavation, a vibrating screen (or other size-separating device), homogenization equipment, conveyors, and, if needed, a rock or soil washing system or a rock crushing unit. The bioreactor requires agitation to stir the soil in the slurry. Equipment to measure the slurry pH, temperature, and redox potential is also necessary to monitor the treatment process.

The time required to excavate, screen, and homogenize the soil with the potato starch prior to forming the slurry in the bioreactor is a function of the soil type, moisture content, and soil volume. In the future, Simplot proposes to homogenize the potato starch with the water prior to the contaminated soil addition. Once the bioreactor has been filled and the monitoring equipment is in place, maintenance requirements are minimal. Access roads are needed for equipment and office trailer transportation. After the treatment is completed, the small portable bioreactor can be emptied, agitators (if any) removed, and all equipment shipped offsite within 3 days. For the cases

of inground pits and large modular bioreactors, upon the completion of treatment, the liner base can be breached (if treatment standards have been met). The walls of the tank can be removed and shipped to the next remediation project.

If the contaminated soil contains volatile organic compounds (VOCs), then some form of cover equipped with a VOC collection device (such as a carbon adsorber) or a treatment device (such as a biofilter) is required during the excavation phase of treatment. The soil stockpiled after excavation should be wetted and covered to minimize airborne emissions.

Utility requirements for this technology include water and electricity. For this SITE Demonstration, lancing (to mix the soil with the water) was required once every 2 wk. Approximately 24,000 L (6,400 gal) of water was required to remediate 23 m³ (30 yd³) of soil. An electrical circuit is required to power the screening equipment, any agitation equipment, or any homogenization requirements. The current needed is a function of the size of the equipment, which in turn depends on the size of the site.

Performance Data

The J.R. Simplot Bioremediation Technology was evaluated to determine its effectiveness in degrading TNT and further destroying any toxic intermediate compounds that may be formed during the treatment process. The critical objective for this Demonstration was to determine the percent reduction of TNT based on the concentration in the pre-treatment slurry on a dry basis compared to the concentration in the post-treatment slurry on a dry basis. Other objectives for this evaluation included:

- to determine the presence of likely intermediate compounds before and after treatment;
- to develop operating costs;
- to determine the relative toxicity of the soil before and after treatment; and
- to monitor the pH, redox potential, and temperature of the slurry throughout the course of treatment.

For the Demonstration Test, 23 m³ (30 yd³) of WSOW soil was excavated and screened. All oversize material (>15.9 mm) was separated and placed in a lined area for further disposition. After this step was performed, 41 primary samples were taken from the screened soil to determine the average TNT concentration. Soil samples were also taken for the analysis of metals, herbicides, pesticides, relative toxicity, grain size distribution, and Atterberg Limits. A total of 24,000 L (6,400 gal) of potable water was added to the bioreactor. This water was sampled and analyzed for the chemical parameters stated above.

Relative toxicity testing of the soil was performed to determine if the treatment process had caused the relative toxicity of the treatment medium to increase because of the degradation of TNT.

After the soil and water had been added to the bioreactor, a sterile process control sample was taken from the bioreactor. The purpose of this sample was to subject it to a required level of gamma radiation to destroy the TNT degraders and then determine, after the treatment had been concluded, if any TNT degradation in the bioreactor was a consequence of biological activity. However, based on total plate counts, it was found that the sample did not receive the required level of gamma radiation and that possibly TNT degraders were still present in the slurry after the irradiation. However, the presence of known intermediate compounds produced during the treatment process strongly indicated that the remediation was biological.

Appropriate anaerobic conditions ($E_h < -200$ mV) were achieved in 26 days. During the biodegradation of TNT, microorganisms break the NO linkage, forming amino groups. This causes the slurry to become alkaline. Therefore, hydrochloric acid was added at intervals to control the pH. After the commencement of treatment, the ambient temperature began to drop. When freezing conditions were encountered, three immersion heaters were added to the bioreactor to try and maintain enough heat suitable for bioremediation.

Daily sampling at five locations within the bioreactor, with analysis by a field TNT test kit and the Method 8330 Short-Run (2), gave an indication of the treatment rate. Figure 2 shows these locations. A plot of the degradation of TNT and the rise and fall of one intermediate compound for one location is given in Figure 3. This figure gives an approximation of the degradation process within the bioreactor. Based on the results of the daily sampling and analysis, the first stage of post-treatment sampling was initiated in February 1994 (day 156). This first stage of post-treatment sampling included 50 primary samples for the analysis of TNT, 5 samples for the levels of intermediate compounds, and final samples for relative toxicity testing.

The results of this first stage of post-treatment sampling showed that the average solid phase concentration of TNT on a wet basis was 54 mg/kg. This was below the set regulatory limit of 57 mg/kg. Two individual aliquots of the treatment soil gave values of TNT much higher than encountered in pre-treatment sampling. It was also found that, in each of 4 locations, the sum of the intermediate compounds exceeded the regulatory guideline of 2.5 mg/kg.

The relative toxicity testing was performed based on this intermediate round of sampling. The conclusions drawn from this round of testing are:

The intermediate-treatment soil had essentially 100% earth-

worm survival across all dilutions. The pre-treatment soil had 0% survival in 100% and 50% dilutions.

The root elongation study showed a consistent relationship of more growth of alfalfa, red clover, cucumber, lettuce, and wheat roots in the intermediate-treatment soil as compared to the pre-treatment soil.

Further results and conclusions regarding the toxicity tests can be found in the Innovative Technology Evaluation Report.

Summary of Results

In September 1993 (day 0), 41 primary samples were taken of the feed soil and 3 primary samples were collected from the make-up water placed in the bioreactor were taken for TNT analysis. From these samples, the average pre-treatment slurry concentration (dry basis) of TNT placed into the bioreactor was 1,500 mg/kg. The final stage of sampling was achieved in late June 1994 (day 283), approximately 9 mo after loading the bioreactor. From the 40 samples collected, the final slurry concentration (dry basis) of TNT in the bioreactor was determined to be 8.7 mg/kg. This is much below the State required limits. Based on this information, the Reduction Efficiency of this process on TNT is determined to be 99.4%. The 95% Confidence Interval associated with this average is 98.3% to 99.9%. The analytical method used to determine this reduction was derived from SW-846 Method 8330 with minor modifications developed by the Army Corps of Engineers. Intermediate compounds formed by the biodegradation of TNT were below the analytical detection limit. No other known derivatives of TNT biodegradation were found in the slurry at the completion of treatment.

Metals concentrations (i.e. aluminum, barium, cadmium, chromium, copper, iron, lead, magnesium, manganese, nickel, vanadium, and zinc) in the pre-treatment soils were at levels generally found in natural soils and were not toxic to the microorganisms. Bioconcentration of the toxic metals did not appear to be occurring in this process as metals concentrations did not change as a result of TNT biodegradation.

A negative control sample which consisted of a 0.02 m³ (5-gal) HDPE pail, 60% full of only pre-treatment soil (no make-up water) was left in the vicinity of the bioreactor. The purpose of this negative control was to determine if the TNT had degraded because of the J.R. Simplot process. Samples were taken for TNT analysis at the beginning and end of the treatment process. Statistically, there was no TNT reduction in the negative control (2), thus showing that the accelerated TNT degradation in the bioreactor was because of the bioremediation technology.

Economic Analysis

Estimates on capital and operating costs have been determined for a treatment volume of 3,824 m³ (5,000 yd³) of TNT-contaminated soil. This cost is estimated to be \$147/m³ (\$112/yd³). This does not include excavation of the TNT-contaminated soil. Economic calculations for this estimate are based on information gathered during the Demonstration at the WSOW site and information provided by Simplot.

The estimated cost will vary depending on contamination level, soil type, site facilities, and site location. This cost is an order-of-magnitude estimate, as defined by the American Association of Cost Engineers, with an expected accuracy within +50% and

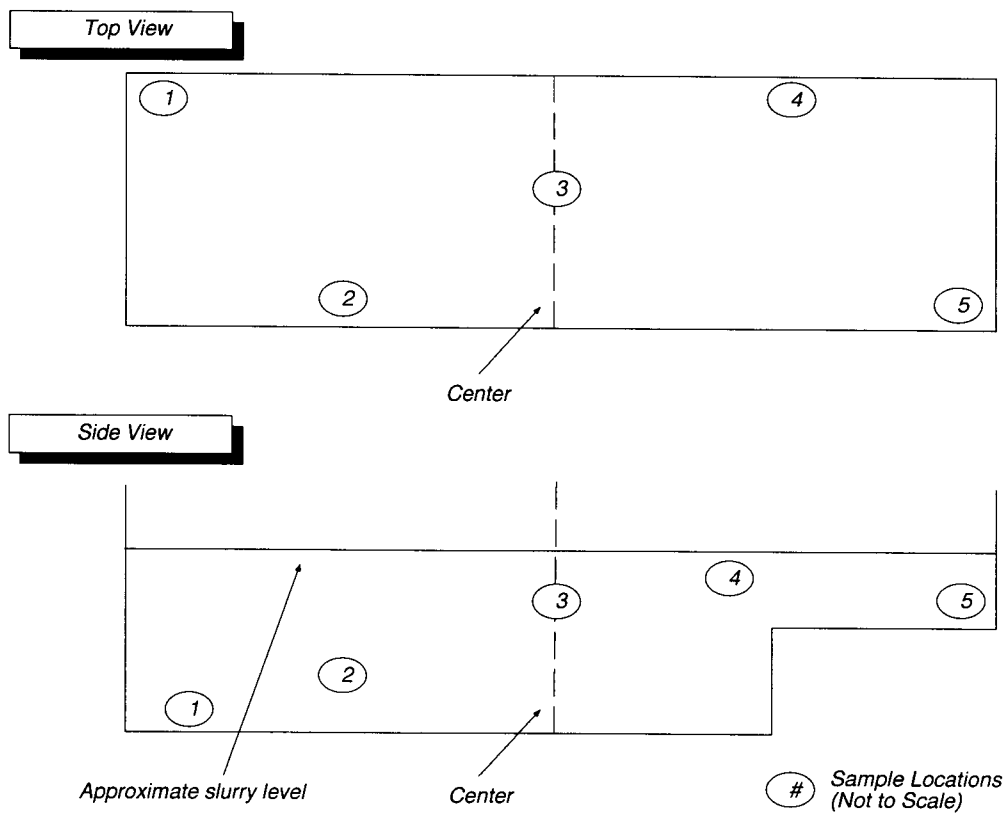


Figure 2. Approximate daily sampling locations for TNT analysis by field kit and the 8330 short-run method.

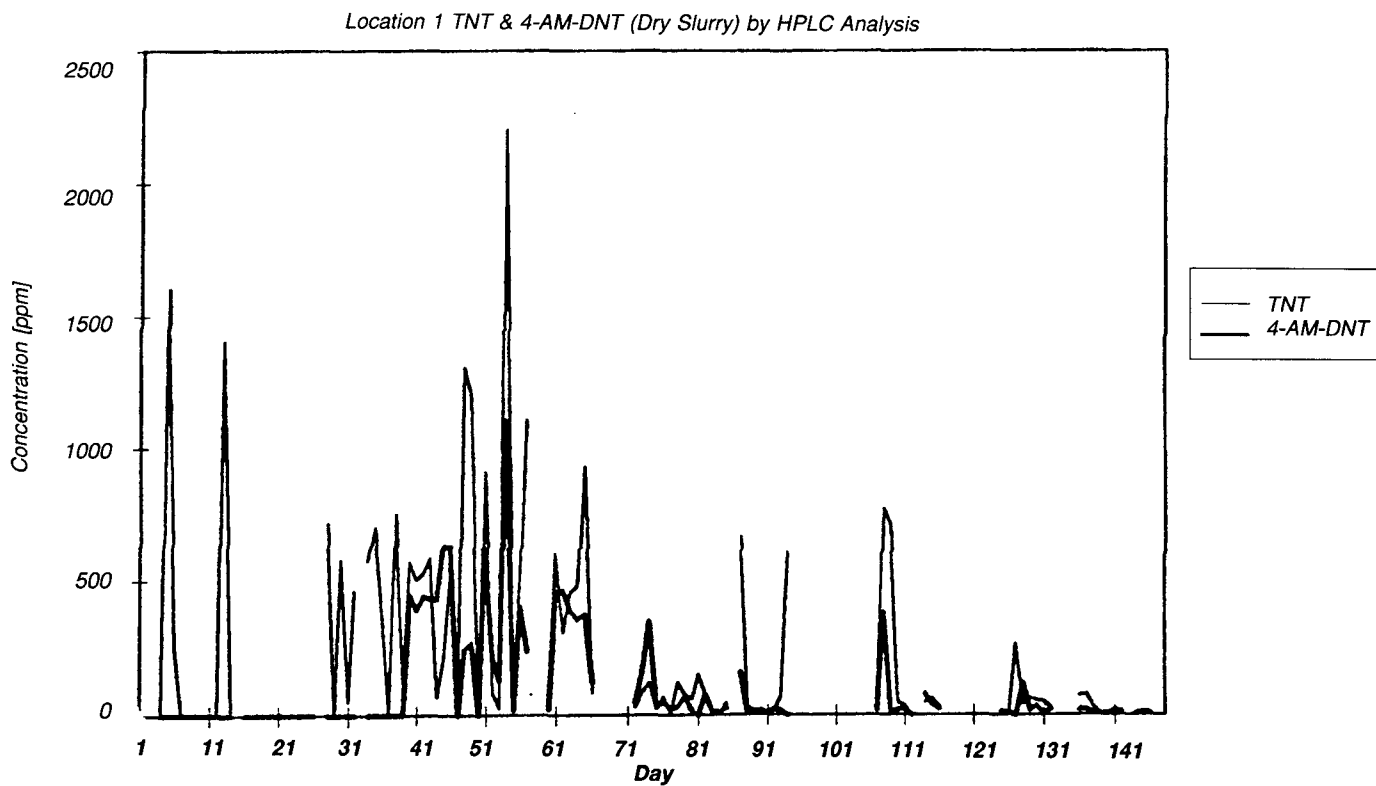


Figure 3. Daily sampling results for location 1.

-30%. Since this is an innovative technology, the range may actually be wider.

The cost for treating approximately 3,824 m³ of TNT-contaminated soil is based on:

- construction of four lined pits, each 15.2 m (50 ft) wide, 104 m (340 ft) long, and 1.2 m (4 ft) deep with a 0.3 m (one ft) berm;
- treatment of TNT-contaminated soils with levels and soil characteristics similar to the Demonstration Test soil;
- a direct scale-up of chemical usage from the SITE Demonstration; and
- a batch treatment time of 6 mo.

If Simplot scales-up its process differently than stated (i.e., using modular bioreactors rather than lined pits), then the cost of remediation per cubic meter of contaminated soil will change.

This cost estimate is representative of charges typically assessed to the client by the vendor and does not include profit. This cost does not include an additional cost that may be charged by the J.R. Simplot Company. Depending on site characteristics, an additional cost of up to \$131/m³ (\$100/yd³) may be assessed to the client for supplemental technical assistance, soil nutrients, a carbon source, and other process enhancements. A detailed explanation of these costs, including the 12 cost categories examined, can be found in the Innovative Technology Evaluation Report.

Technology Status

The University of Idaho, in cooperation with the J.R. Simplot Company, has ongoing research programs to design improvements in the Simplot process and expand the applicability of this technology to specific sites and for additional compounds. Further work is being conducted by the University of Idaho and the Environmental Protection Agency to develop an in-situ process for subsurface soils and groundwater.

Currently, treatability studies are being performed on soil from several sites contaminated with TNT and other explosives in addition to sites contaminated with the herbicide, dinoseb. Work plans are being developed to obtain regulatory agency approval for full-scale remediations to begin in the spring of 1995. The Idaho Department of Environmental Quality has approved the use of the process at a dinoseb-contaminated site near Pocatello, ID. After the SITE Demonstration Test, full-scale remediation of the dinoseb-contaminated site near Ellensburg, WA is scheduled for the Spring of 1995. Approval from the California Department of Toxic Substance Control is required before the process can remediate a site in Reedley, CA. Field-scale remediation at Reedley has proven highly effective, and it is anticipated that full-scale remediation will begin in 1995.

Additional laboratory treatability studies are being performed using the Simplot process on explosives-contaminated soil from several U.S. Navy bases by the Corps of Engineers

Waterways Experiment Station in Vicksburg, MS. Additional laboratory studies are underway to determine the suitability of the process to treat explosives-contaminated soil from a former ordnance works near Mead, NE. Additionally, inground pits are being constructed for testing the process on soil contaminated with explosive compounds at Bangor Submarine Base near Seattle, WA.

SITE Program

In 1980, U.S. Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund. CERCLA was amended by the Superfund Amendments and Reauthorization Act (SARA) in 1986. The SITE Program is a formal program established in response to SARA. The primary purpose of the SITE Program is to maximize the use of alternatives in cleaning up hazardous waste sites by encouraging the development and demonstration of new, innovative treatment and monitoring technologies. It consists of four major elements: the Demonstration Program, the Emerging Technology Program, the Measurement and Monitoring Technologies Program, and the Technology Transfer Program. The J.R. Simplot Ex-Situ Bioremediation Technology was evaluated under the Demonstration Program. This Capsule was published as part of the Technology Transfer Program.

Disclaimer

While the technology conclusions presented in this report may not change, the data has not been reviewed by the Quality Assurance/Quality Control Office.

Sources of Further Information

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